Probing Multi-Scale Energy Landscapes Using the String Method

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A novel and powerful method is presented for the study of rare switching events in complex systems with multiscale energy landscapes. The method performs an umbrella sampling of the equilibrium distribution of the system in hyperplanes normal to the effective transition pathway, i.e. the transition pathway of a coarse-grained potential which need not to be known beforehand. Rather the effective transition pathway is determined on the fly in an adaptive way by evolving a smooth curve, called a string, that connects the initial and final regions and feels thermally averaged potential forces. Appropriate averages around the string determine the transition rates. Application to an example of solid-solid transformation of a condensed system is presented.

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The evolution of complex systems often involves widely separated time scales. Well-known examples include nucleation events during phase transition, conformational changes of macromolecules, and chemical reactions. The separation of time scale is a consequence of the disparity between the effective thermal energy and typical energy barrier of the systems. The state of the system is confined for long periods of time in metastable regions in configuration space and only rarely switches from one region to another. The dynamics of the system effectively reduces to a Markov chain on the metastables regions. Finding the transition rates between the metastable states is a major computational challenge. For low dimensional systems, pathways and rates can be determined by identifying the minimal energy paths (MEPs) which connect different minima on the energy surface by going through saddle points, and the curvature around these paths. For higher dimensional systems, such a procedure becomes impractical since the energy surfaces is typically dense in critical points and a multitude of dynamic paths contribute to the transition. The transition pathways have to be understood in an averaged sense as the superposition of the many paths by which transition between two metastable regions in phase space takes place.

Sophisticated numerical techniques have been developed for finding transition pathways and rates [1, 2, 3], though most methods apply when the energy landscape is relatively smooth (e.g. when transition is accomplished by a few isolated MEPs), and become less useful otherwise. A notable exception is the transition path sampling technique (TPS) [3] which applies to situations when the potentials are multiscaled. TPS samples the probability of dynamical trajectories conditional on their end points being in given regions of the configuration space. The transition rates are determined by reconstructing the unconditional probability of the trajectories through umbrella sampling of trajectories whose end points are constrained in overlapping sub-regions covering configuration space. TPS computes rates directly (i.e. without relating them to the geometry of the potential). In this Letter, we propose an alternative approach which performs an umbrella sampling of the equilibrium distribution of the system in hyperplanes normal to the transition pathways of a coarse-grained potential which need not be determined beforehand. Appropriate averages then determine the transition rates.

We shall focus on the example of a system modeled by

$$\gamma \dot{q} = -\nabla V(q) + \xi(t) \tag{1}$$

where γ is the friction coefficient and $\xi(t)$ is a white noise with $\langle \xi_j(t)\xi_k(0)\rangle = 2\gamma k_B T \delta_{jk}\delta(t)$. In molecular dynamics, (1) is the high friction (or Smoluchowski) limit, but the method can be generalized easily to arbitrary friction. We assume that the potential $V(q)$ is multi-scaled in the sense that there is a gap between $k_B T$ and the relevant energy barriers of the system. The system may certainly have other energy barriers that are comparable or smaller than $k_B T$. In this case, even though V may contain a very large number of local minima, the system experiences a much smoother energy landscape because of thermal effects and we are interested in the "thermally averaged" energy landscape: $\overline{V} := \langle V \rangle$. The dynamics in both V and $\overline{V}$ reduce to the same Markov chain on suitable metastable basins separated by the large energy barriers. In principle, one can study the transitions in such systems by first computing $\overline{V}$ and then applying methods for smooth energy landscapes such as the nudged elastic band (NEB) method [2] or the zero-temperature string method [4] to study the transition in the system with potential $\overline{V}$. But in practice it is often impossible to first find $\overline{V}$. The motivation of the present paper is to develop a method that is based directly on V but computes the *effective* transition pathways and rates associated with $\overline{V}$. This is accomplished by a simple but important modification of the string method introduced in [4] by incorporating thermal averages. The thermal average can either be the result of finite temperature, or the effect of noise introduced numerically to smooth out the small scale features of the energy landscape.

It is useful to first review the zero-temperature string

method [4]. Let φ be a smooth curve, which we call a string, connecting two minima of V, A and B. By definition, φ is a MEP if

$$0 = (\nabla V(\varphi))^{\perp}, \tag{2}$$

where $(\nabla V)^{\perp} = \nabla V - (\nabla V \cdot \hat{t})\hat{t}$ and $\hat{t}$ is the unit tangent vector along φ, $\hat{t} = \varphi_\alpha/|\varphi_\alpha|$. Equivalently φ is a curve which minimizes V in the hyperplane normal to itself. We will use suitable parametrizations of the string such that $\alpha = 0$ at A, $\alpha = 1$ at B. One way of finding solutions of (2) is to follow the dynamics defined by:

$$\varphi_t = -(\nabla V(\varphi))^{\perp} + r\hat{t}. \tag{3}$$

where for convenience we renormalized time as $t \to t/\gamma$. The scalar field $r \equiv r(\alpha, t)$ is a Lagrange multiplier term added in (3) to preserve some constraint on the parametrization of φ. For instance, a simple choice is to impose that φ be parametrized by normalized arclength. In this case (3) must be supplemented by the constraint $(|\varphi_\alpha|)_\alpha = 0$ which determines r. Other parametrizations – for instance by energy-weighted arclength – can be straightforwardly implemented by modifying this constraint. See [4] for details.

This method is very effective if the energy landscape is smooth, as shown in [4]. In this case, it bears a lot of similarity with NEB [2]. But as we now show, it is the differences between the string method and NEB, namely the use of continuous curves with fixed and intrinsic parametrization, that allows us to extend the string method to the case of rough energy surfaces.

When the energy landscape is multiscaled, our objective is to compute the effective transition pathways (MEPs in $\overline{V}$) and rates, without computing first $\overline{V}$. (Let us emphasis that since $\overline{V}$ is relatively smooth and the energy barriers associated with $\overline{V}$ are much larger than k_BT, we can assume that the effective MEPs are isolated.) To this end, we make an important modification of (3), namely we replace the gradient of V at the right hand side of (3) by an ensemble and/or temporal average of the actual force among a number of string configurations. We denote this ensemble by $\{\varphi^\omega\}$, its mean by $\varphi^\circ := \langle\varphi^\omega\rangle$, and therefore replace (3) by

$$\varphi^\circ_t = -\langle\nabla V(\varphi^\omega)\rangle^{\perp,\circ} + r^\circ\hat{t}^\circ, \tag{4}$$

where $\hat{t}^\circ$ is the unit tangent vector along φ° and $(\cdot)^{\perp,\circ}$ denotes the projection to the hyperplane normal to $\hat{t}^\circ$. To preserve parametrization of φ°, (4) must be supplemented by some appropriate constraint which determines r°: for instance, the constraint $(|\varphi^\circ_\alpha|)_\alpha = 0$ corresponds to normalized arc-length.

A practical way to create the ensemble $\{\varphi^\omega\}$ is to introduce a finite temperature version of (3) through

$$\varphi^\omega_t = -(\nabla V(\varphi^\omega))^{\perp,\circ} + r^\circ\hat{t}^\circ + (\eta^\omega)^{\perp,\circ}, \tag{5}$$

where η^ω is a noise term added in order to simulate the effect of thermal averaging. We take η^ω to be a Gaussian process with covariance

$$\langle\eta^\omega_j(\alpha,t)\eta^\omega_k(\alpha',0)\rangle = \begin{cases} 2k_BT\delta_{jk}\delta(t) & \text{if } \alpha = \alpha', \\ 0 & \text{otherwise,} \end{cases} \tag{6}$$

and compute all averages with respect to the statistics of η^ω. In particular, the mean of (5) is (4).

The equilibrium density function for (5) is given by

$$\mu(q,\alpha) = Z^{-1}(\alpha)e^{-\beta V(q)}\delta_{S^\circ(\alpha)}(q). \tag{7}$$

Here $\beta = 1/k_BT$, $S^\circ(\alpha)$ is the hyperplane normal to $\varphi^\circ(\alpha)$, $\delta_{S^\circ(\alpha)}(q)$ is the Dirac distribution concentrated on $S^\circ(\alpha)$, and

$$Z(\alpha) = \int_{S^\circ(\alpha)} e^{-\beta V(q)}d^dq \tag{8}$$

is the partition function. (7) can be determined by analyzing the Fokker Planck equation associated with (5). The mean string $\varphi^\circ(\alpha)$ entering (7) through $S^\circ(\alpha)$ has to be determined self-consistently from

$$\varphi^\circ(\alpha) = \int_{\mathbb{R}^d} q\mu(q,\alpha)d^dq. \tag{9}$$

This equation implies that φ° is a MEP for $\overline{V}$ to leading order in k_BT. Indeed if $V = \overline{V} + \delta V$ with δV comparable to k_BT or smaller, the integral in (9) can be evaluated by Laplace method and to leading order in k_BT, only $\overline{V}$ contributes. This shows that φ° is the minimum of $\overline{V}(q)$ in the hyperplane perpendicular to φ°.

(7) shows that the stochastic string performs an umbrella sampling of the equilibrium distribution of the system in the one-parameter family of hyperplanes normal to a MEP of $\overline{V}$. (We stress again that this MEP needs not be known beforehand but rather is determined on the fly by the method.) Averages with respect to (7) yield relevant quantities like, in particular, the transition rates between the basins of metastability visited by the mean string. This follows from a straightforward generalization of Kramers argument (see e.g. chap. 9 in [5]) to multiscale energy landscapes. Let $F(\alpha) = -k_BT\ln Z(\alpha)$ be the free energy. Using the identity $\int \partial \ln Z/\partial\alpha d\alpha = \ln Z(\alpha)$, we obtain from (8) after integration by part

$$F(\alpha) = \int\left\langle(\hat{t}^\circ\cdot\nabla V)\left((\hat{t}^\circ\cdot\varphi^\circ)_\alpha - \hat{t}^\circ_\alpha\cdot\varphi\right)\right\rangle d\alpha. \tag{10}$$

Let α_1, α_2, ... be the successive values of α where F reaches a local minimum. Each α_j corresponds to a basin of metastability visited by the mean string. Let α_{12}, α_{23}, ... be the successive values of α where F reaches a local maximum. Then

$$k^{-1}_{1\to 2} = 2\gamma\beta\int_{\alpha_1}^{\alpha_{12}} e^{-\beta F(\alpha)}|\varphi^\circ_\alpha|d\alpha\int_{\alpha_1}^{\alpha_2} e^{\beta F(\alpha)}|\varphi^\circ_\alpha|d\alpha,$$

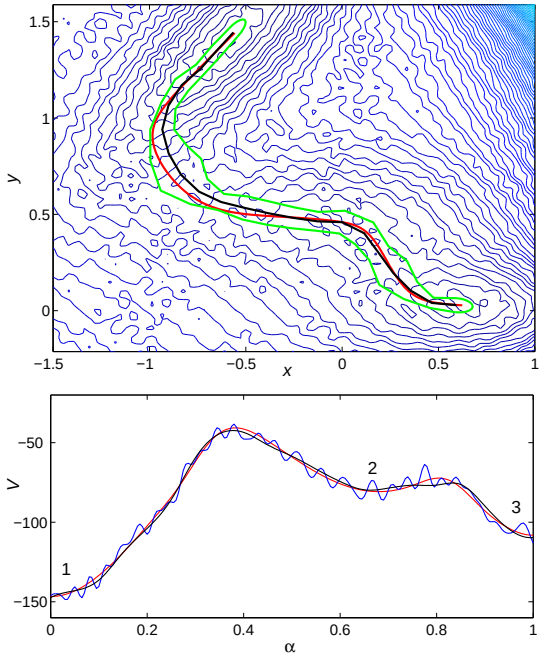

FIG. 1: Upper panel: the mean transition path φ° (black curve) on the disordered Mueller potential isolines. Also shown is the MEP, $\varphi^\star$, in $\bar{V}$ (red curve) obtained by integrating (3). Both curves coincide fairly well as expected. The region within the green curve is the root mean square displacement of the stochastic string indicating the typical size of the fluctuations of the string. Lower panel: the mean energy along the stochastic string (black curve), $\langle V(\varphi)\rangle$, compared with the smoothed energy along the MEP of $\bar{V}$, $\bar{V}(\varphi^\star)$ (red curve). The blue curve is the total energy along φ°, $V(\varphi^\circ)$, which shows the large number of (irrelevant) minima and saddle points crossed during a transition. We took 21 discretization points along the stochastic string and 20 realizations.

and so on. To leading order in k_BT, this expression is equivalent to

$$k_{1\to 2} = \frac{\sqrt{F_{\alpha\alpha}(\alpha_1)|F_{\alpha\alpha}(\alpha_{12})|}}{2\pi\gamma|\varphi^\circ_\alpha(\alpha_1)||\varphi^\circ_\alpha(\alpha_{12})|} e^{-\beta\Delta F_{12}} \qquad (11)$$

where $\Delta F_{12} := F(\alpha_{12}) - F(\alpha_1)$ is the free energy barrier from basin 1 to basin 2.

In practice, (5) is solved by considering M realizations of the string, φ^j, $j = 1, \ldots, M$, and approximating the mean string as $\varphi^\circ = M^{-1}\sum_{j=1}^M \varphi^j$. After a number of steps, a reparametrization step for φ° is applied. Once φ° has converged to its steady state value, no reparametrization step is necessary anymore and, using ergodicity, one can supplement the ensemble average by a time average using $\varphi^\circ = (MT)^{-1}\sum_{j=1}^M \int_0^T \varphi^j(t)dt$ to obtain better statistics. Other averages like (10) are evaluated similarly.

As a first illustrative example of the procedure, we consider a disordered version of Mueller potential. We take $\overline{V}$ to be the Mueller potential, originally invented as a nontrivial test for reaction path algorithms [6], and δV as

$$\delta V(x,y) = \sum_{k_1,k_2=5}^{10} \big(\alpha_k \cos(2\pi(k_1 x + k_2 y)) + \beta_k \cos(2\pi(k_1 x - k_2 y))\big), \qquad (12)$$

where $\alpha_k, \beta_k \in [-1, 1]$. With this choice $|\delta V| \le 10$ (compared to a main energy barrier of about 100 in $\bar{V}$) and we shall assume that $k_BT = 5$. The number of MEPs in $V = \bar{V} + \delta V$ joining the regions of metastability around the two deeper minima of $\bar{V}$ is of the order of 10^2. This makes the complete sampling of the MEPs in V (say, using (3) with the full V, or NEB) impractical (and irrelevant). The results of the stochastic string method are summarized in figure 1. The MEP in $\bar{V}$ is successfully retrieved and, using (10), we also obtained the value $\Delta F_{12} = 109.0$ for the free energy barrier between 1 and 2, compared to the exact value of $\Delta F_{12} = 108.9$ [7].

Our next example illustrates the complex energy landscapes for systems in condensed phases. We consider a crystal of 20×20 array of atoms interacting via a pairwise potential that has three minima at $r_1 = 1, r_2 = 1.1$ and $r_3 = \sqrt{1 + 1.1^2}$. There are two basic equilibrium states for this systems, with the position of the (i, j)-th atom given by $(r_1 i, r_2 j)$ and $(r_2 i, r_1 j)$ respectively. Their rigid body rotations are considered to be equivalent states. The two states can be considered as the two variants of the martensitic phase. We are interested in the energy landscape that the system experiences when transforming from one variant to the other.

For clarity we initiate the seed of transformation at the upper-left corner. Free boundary conditions are used in the simulation. The crystal transforms through the propagation of the twin boundary, oriented diagonally as shown in Figure 2. The twin boundary propagates through kink propagation along the twin boundary associated with the phase transformation of individual atoms. The energy landscape exhibits three scales: The largest scale associated with the position of the twin boundary, an intermediate scale associated with the propagation of the twin boundary by one atomic distance, and a small scale associated with the kink propagation. For the stochastic string method, we choose k_BT to be in between the energy barrier for kink propagation and twin boundary propagation. The energy landscape for the twin boundary to advance one atomic distance is shown in Figure 2. 40 points are used. In Figure 2 we also show the potential energy landscape associated with the MEP computed using the deterministic string method with 400 points. Even though the details of the energy landscape is not resolved, as expected, the overall feature is captured very well by the stochastic string method using only 40 points.

In conclusion, we have introduced a powerful method to probe multiscale energy landscape and thereby determine effective transition pathways, free energy barriers,

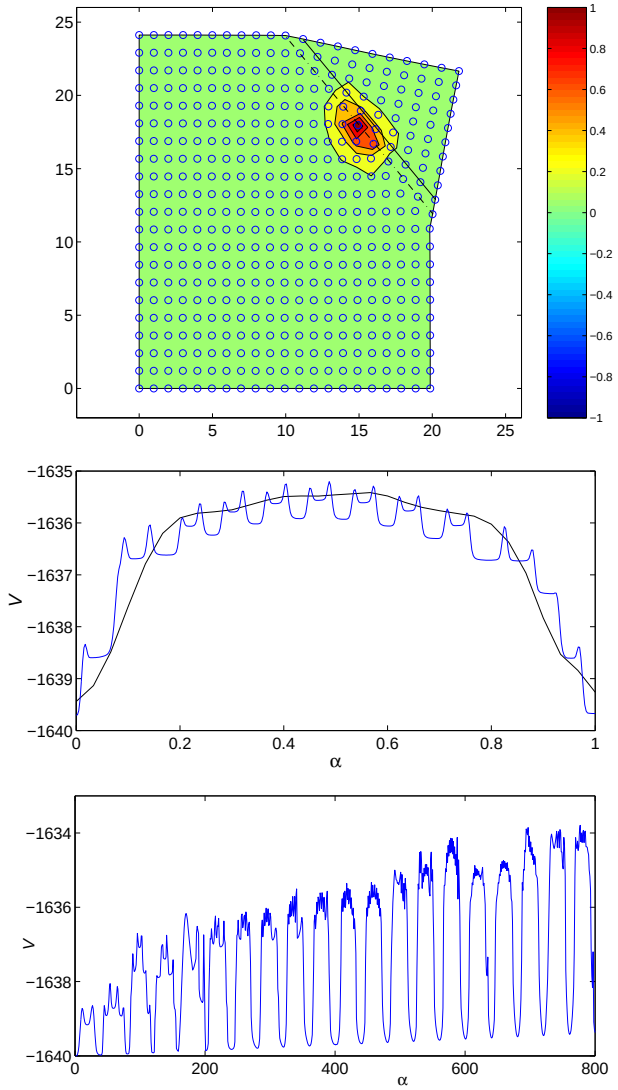

FIG. 2: Upper panel: Snapshot of the crystal during transformation. The color bar shows the scale of the local energy of each atom. Middle panel: The mean potential, $\langle V(\varphi)\rangle$, experienced by the crystal at finite temperature when the twin boundary moves by one atomic distance along the diagonal. This result was obtained using 40 discretization points along the strings. Also shown for comparison is the potential energy along one particular MEP (blue curve, at zero temperature) which shows the features of the potential associated with the transformation of individual atoms along the twin boundary. 400 discretization points along the string were necessary to get this fully resolved result. Lower panel: The energy landscape computed by the string method at finite temperature after the crystal is half transformed. Notice the appearance of three scales on the energy landscape.

and transition rates in complex systems. The method performs umbrella sampling in the hyperplanes perpendicular to an effective transition pathway which is determined on the fly in an adaptive way. The method can be further improved in various ways. For instance the temperature of the string can be periodically changed on an annealing schedule. This allows to further explore the energy landscape and determine if more than one effective transition pathway is involved in a given transition. We are also investigating the possibility of using Metropolis Monte-Carlo scheme instead of the Langevin equation (5) to compute averages with respect to the equilibrium distribution in (7). This speeds up convergence since it requires to compute V only instead of its gradient. Finally, in its present form the method performs the coarse-graining in an implicit way, i.e. no reaction coordinate has to be known beforehand. In certain systems where reaction coordinates can be easily determined, the method can be applied to these coarse-grained variables alone, which might dramatically speed up convergence if the reaction coordinates are low dimensional.

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[1] I. V. Ionova, E. A. Carter, J. Chem. Phys. **98**, 6377 (1993); R. Olender and R. Elber, J. Chem. Phys. **105**, 929 (1996); Theochem.–J. Mol. Struc. **398**, 63 (1997); A. Michalak and T. Ziegler, J. Phys. Chem. A **105**, 4333 (2001); D. Passerone and M. Parrinello, Phys. Rev. Lett. **87**, 108302 (2001).

[2] H. Jónsson, G. Mills, and K. W. Jacobsen, in: Classical and Quantum Dynamics in Condensed Phase Simulations, B. J. Berne *et al.* eds, World Scientific, 1998; G. Henkelman and H. Jónsson, J. Chem. Phys. **113**, 9978 (2000).

[3] C. Dellago, P. G. Bolhuis, F. S. Csajka, and D. Chandler, J. Chem. Phys. **108**, 1964 (1998); C. Dellago, P. G. Bolhuis, and D. Chandler, J. Chem. Phys. **108**, 9236 (1998).

[4] W. E, W. Ren, and E. Vanden-Eijnden, submitted to: Phys. Rev. B (available electronically at: arXiv.org/abs/cond-mat/0205527).

[5] C. W. Gardiner, Handbook of Stochastic Methods, 2nd ed. Springer, 1985.

[6] K. Mueller, Angew. Chem. **19**, 1 (1980); K. Mueller and L. D. Brown, Theor. Chim. Acta **53**, 78 (1979).

[7] The exact value for the free energy barrier is obtained by determining the MEP in the smooth Mueller potential $\overline{V}$, the energy barrier along this MEP, and the determinant of the Hessian at the minima and saddle points.